

Studying interfaces and other buried things with X-ray emission spectroscopy

Clemens Heske
Department of Chemistry
University of Nevada, Las Vegas

heske@unlv.nevada.edu

Coauthors

O. Fuchs, L. Weinhardt, U. Groh, D. Eich, and E. Umbach,
Experimentelle Physik II, Universität Würzburg

M. Keim, G. Reuscher, A. Waag, and G. Landwehr,
Experimentelle Physik III, Universität Würzburg

A. Fleszar, Theoretische Physik I, Universität Würzburg

Ch.-H. Fischer and M.Ch. Lux-Steiner, Hahn-Meitner-Institut,
Berlin

S. Zweigart, W. Riedl, and F. Karg, Siemens & Shell Solar,
München

J.D. Denlinger, Advanced Light Source, Berkeley

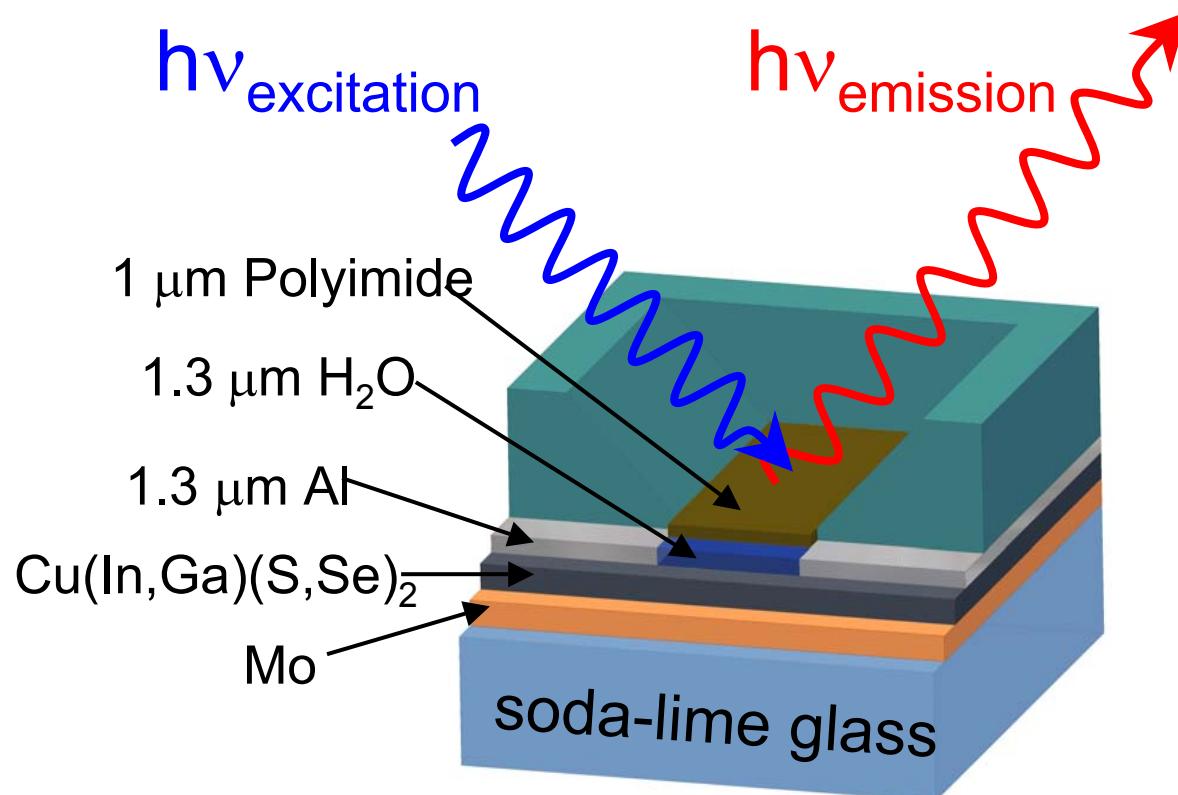
Outline

- XES of liquid-solid interfaces:
water on Cu(In,Ga)(S,Se)₂ solar cell
absorbers
- Resonant XES of liquids: H₂O and D₂O
- RIXS of Be chalcogenides „under cover“

Motivation

- Why XES of solid-liquid interfaces ?
 - electronic structure of valence electrons
 - atom specific
 - chemically sensitive
 - Photon-in-photon-out: bulk and interface information
- Why $\text{H}_2\text{O}/\text{Cu}(\text{In},\text{Ga})(\text{S},\text{Se})_2$?
 - Thin film solar cells with high efficiency ($\eta = 19.2 \%$)
 - Coating processes in a chemical bath
 - Influence of humidity ?

XES of the H₂O/CIGSSe interface



XES of various sulfur compounds

Peak identification:

(1): S 3s → S 2p sulfide

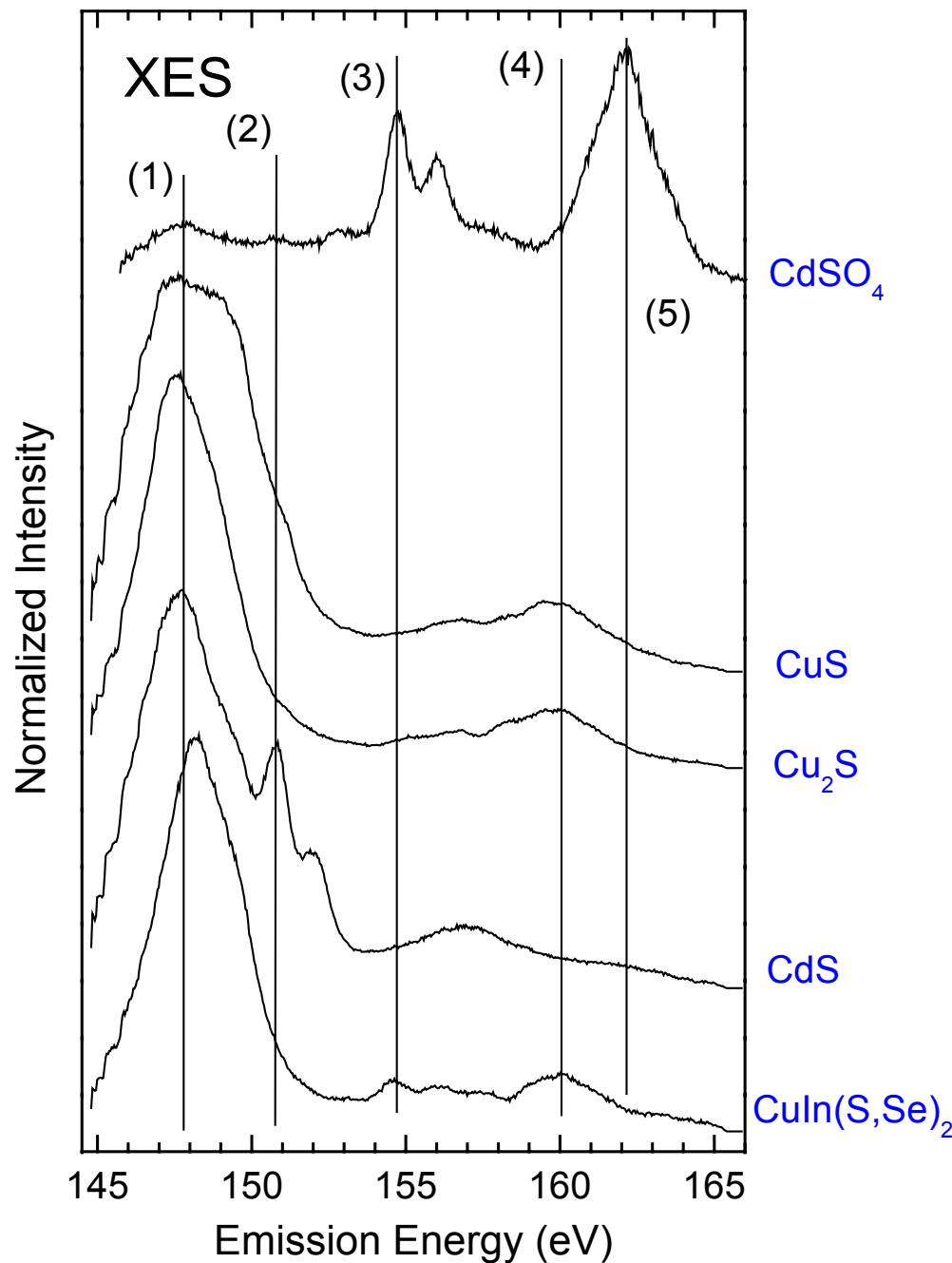
(2): Cd 4d → S 2p S-Cd bonds

(3): S 3s → S 2p S-O bonds
In 5s → S 2p S-In bonds

(4): Cu 3d → S 2p S-Cu bonds

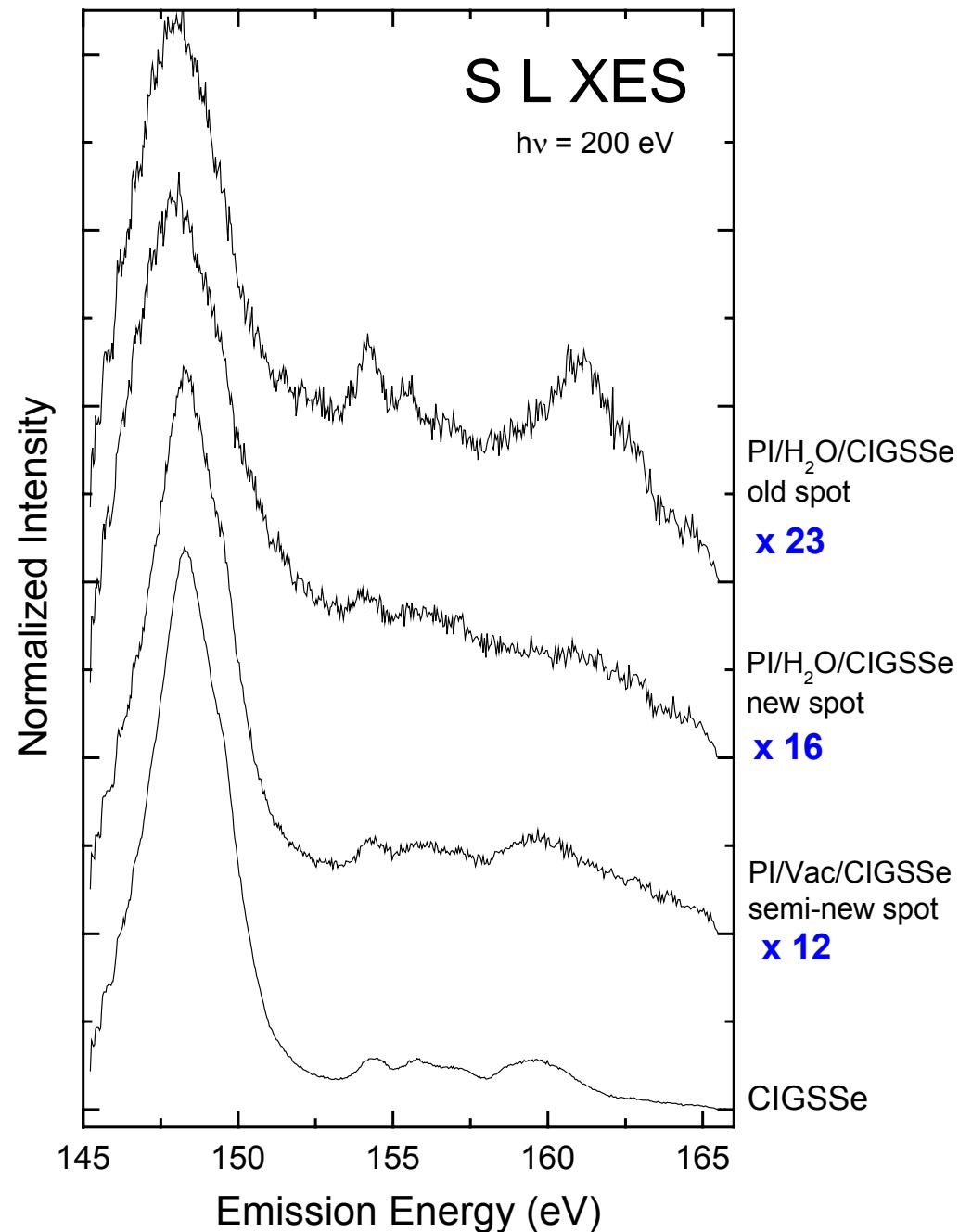
(5): S 3d → S 2p S-O bonds

→ Local environment of sulfur atoms can be identified !



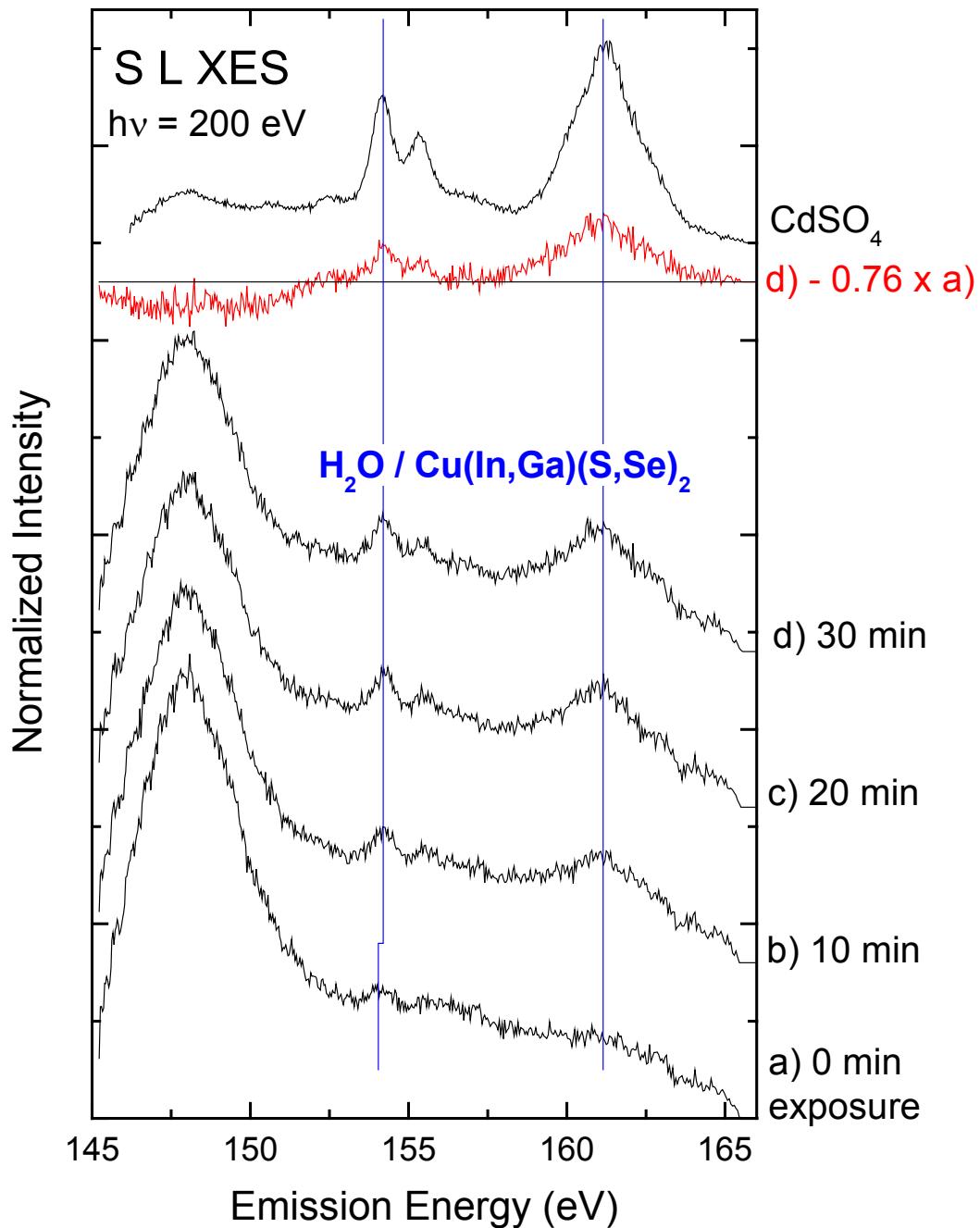
signal attenuation

- Attenuation through 1 μm polyimide (PI) and 1.3 μm H_2O is "bearable"
- PI is altered by X-ray beam
- Chemical reaction: one-day presence of water reduces Cu-S bonds !



$S\ L_{\alpha}$ XES

- Chemical reaction:
X-ray beam stimulates sulfate formation !
- Sulfate formation is local:
new sample position gives pristine spectrum !

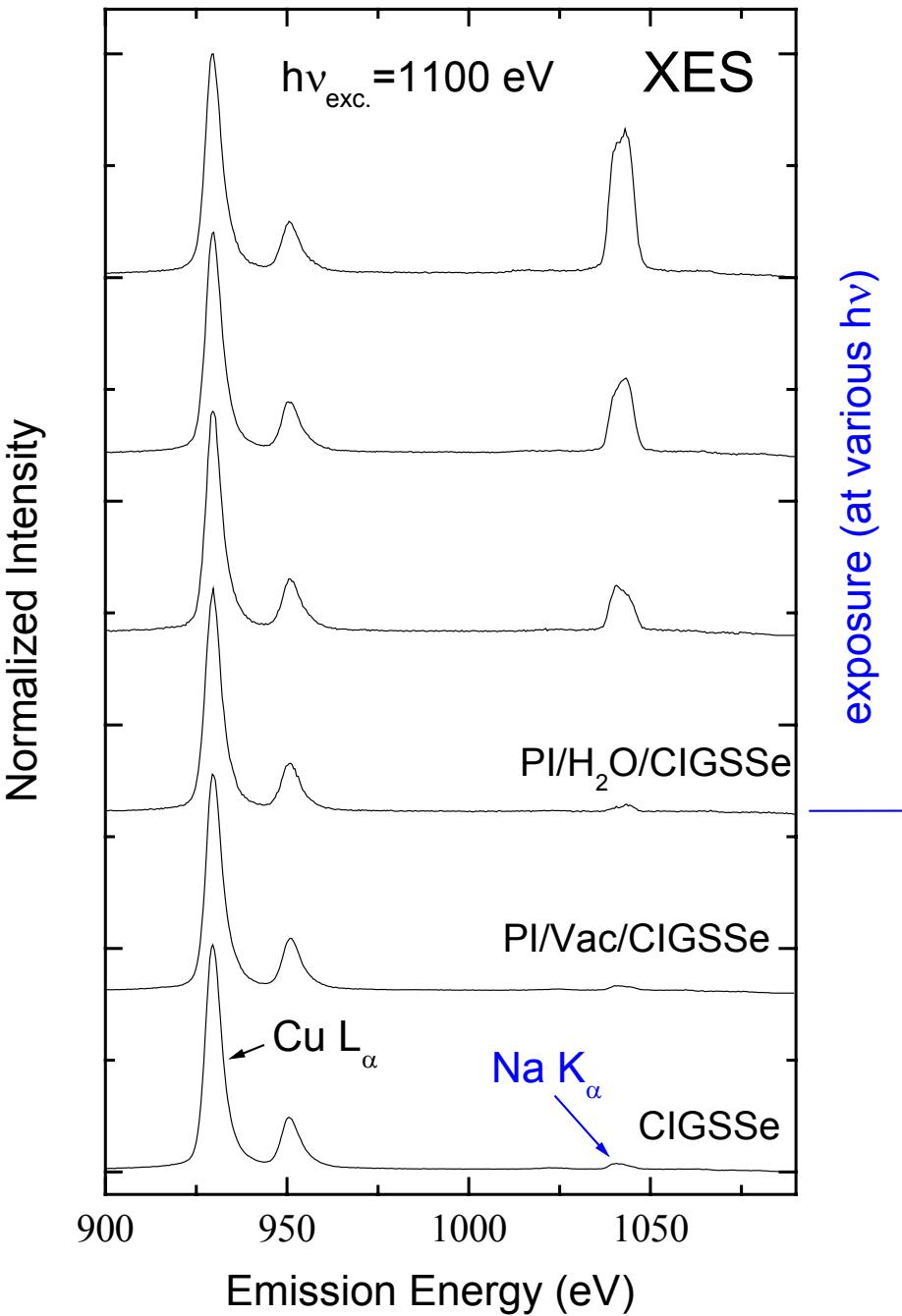


Na and Cu XES

- During the sulfate formation: Na signal is strongly increased !

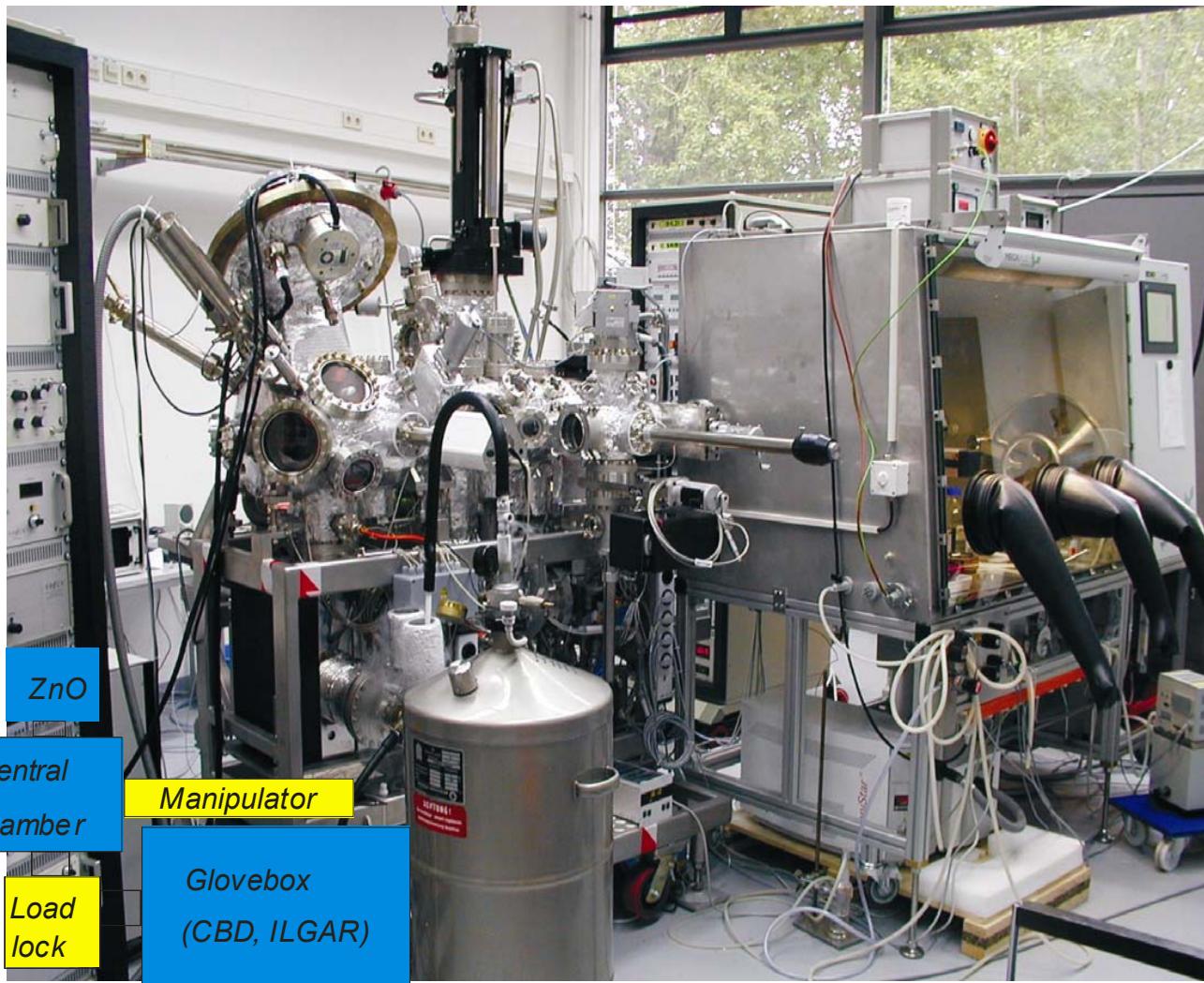
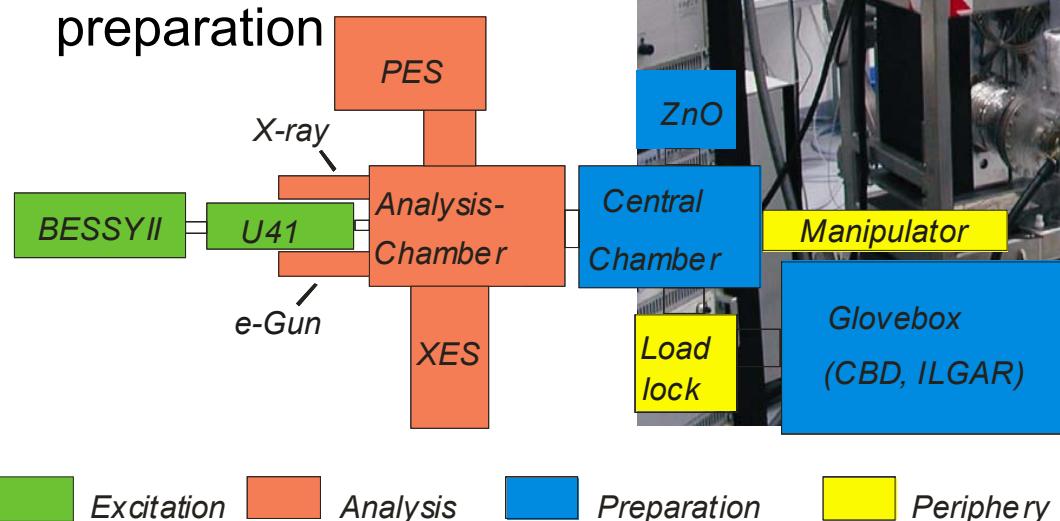
⇒ direct correlation between Na and water !

(this is important for the solar cells: Na is known to enhance the performance)

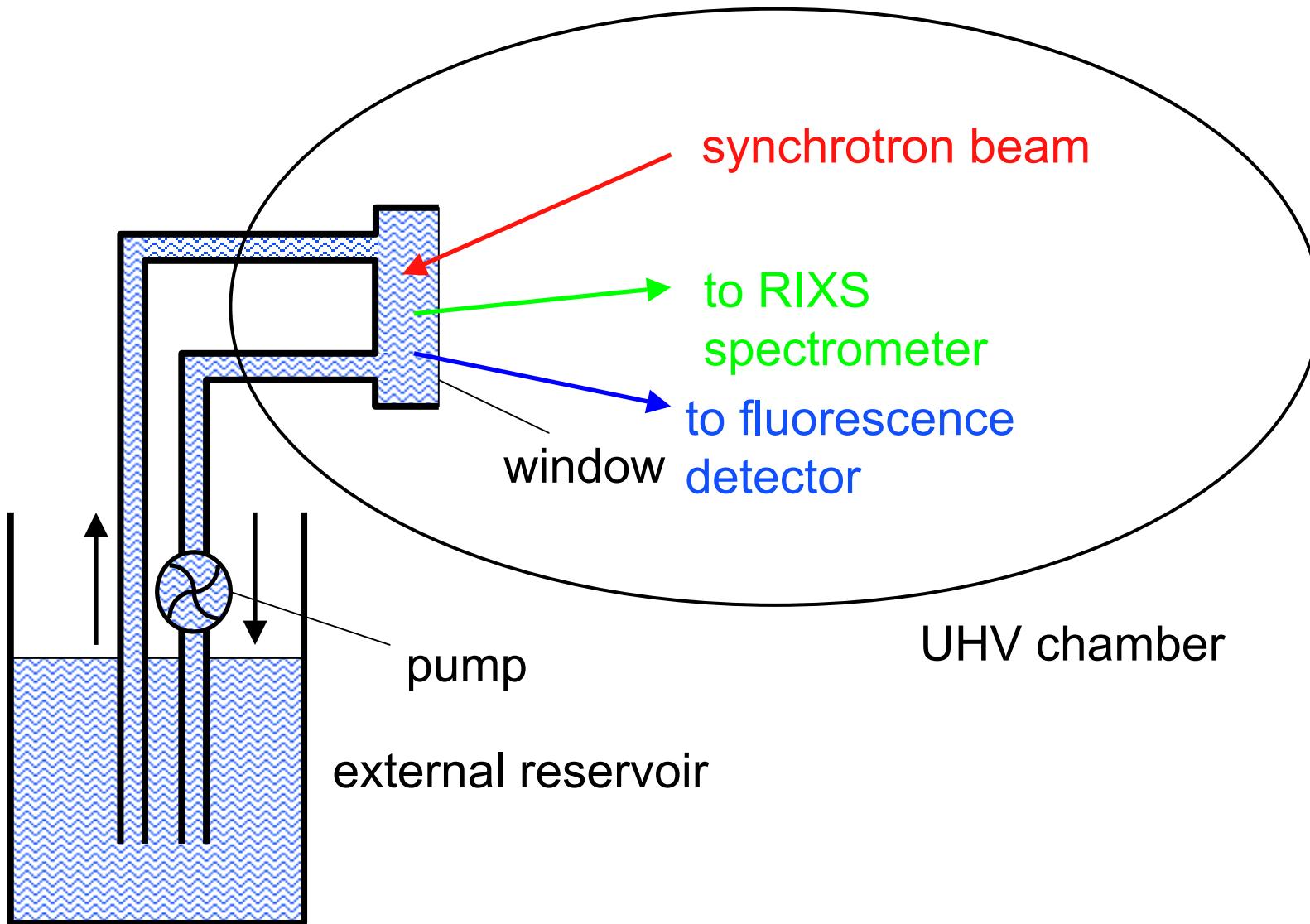


CISSY: Cu(In,Ga)(S,Se)₂ diagnostics with synchrotron radiation

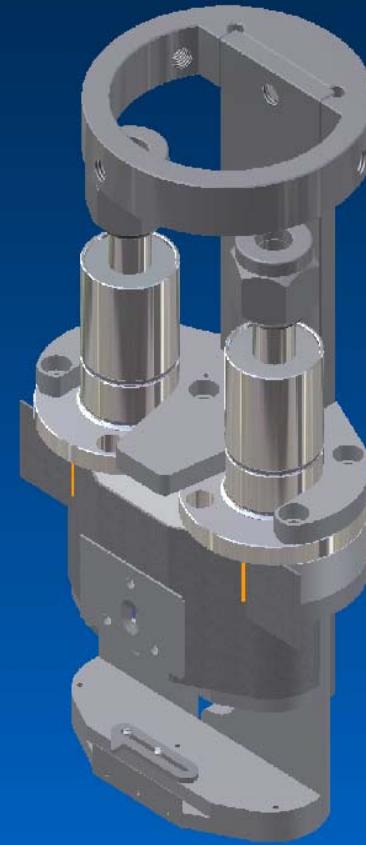
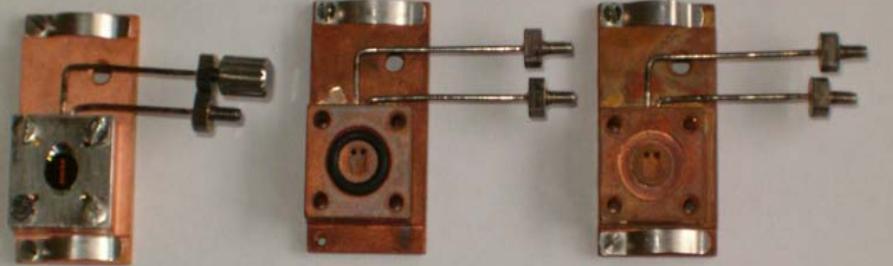
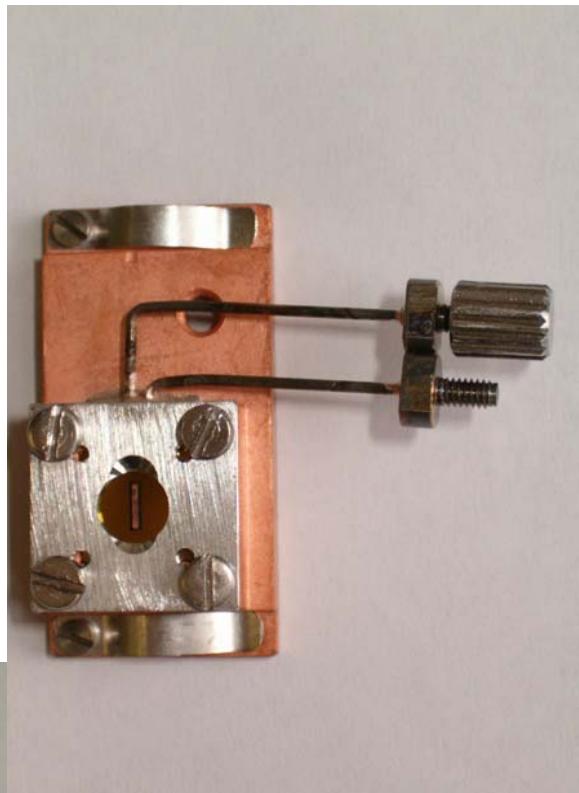
- In-system preparation:
ZnO sputter deposition
wet chemical deposition
in-situ wet cells
- X-ray emission (XES)
- Photoemission (PES)
- Various lab techniques (XPS, UPS, ISS, ...)
- Next: Cu(In,Ga)(S,Se)₂ preparation



X-ray absorption and emission spectroscopy of liquids

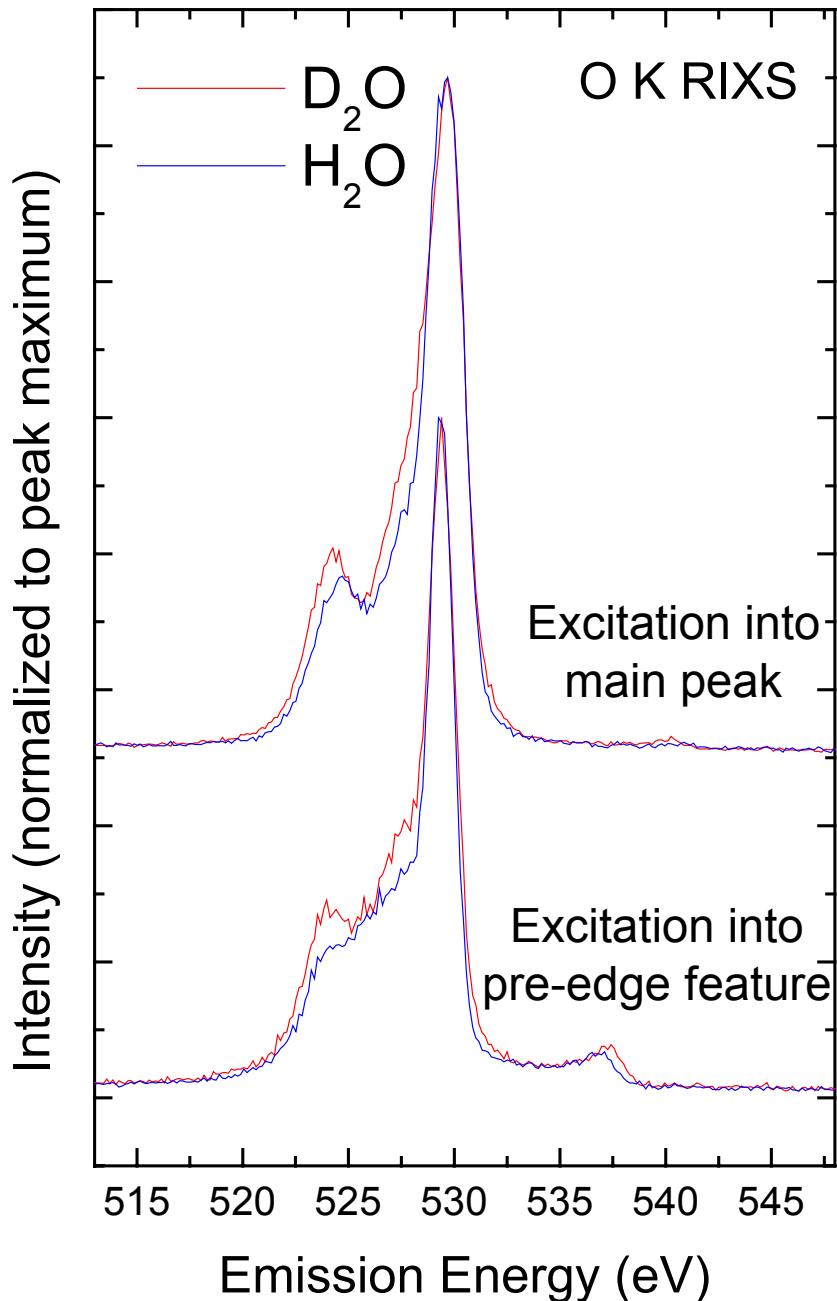
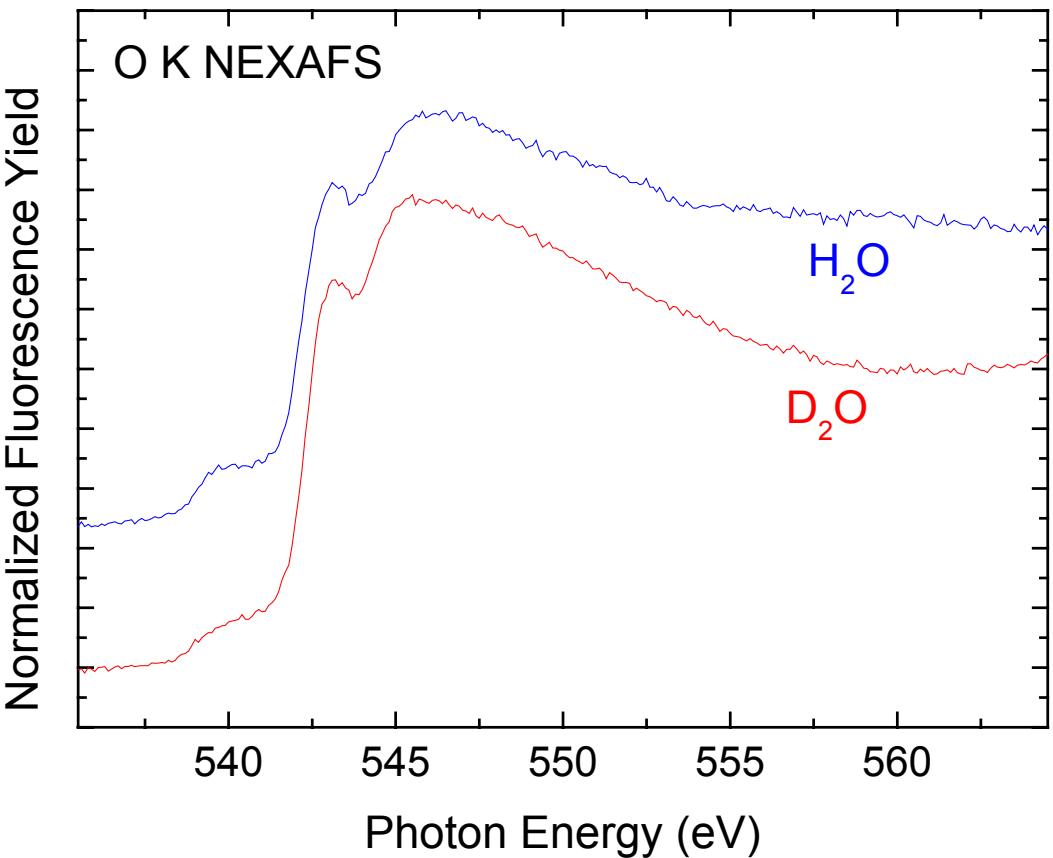


Real-world wet cells

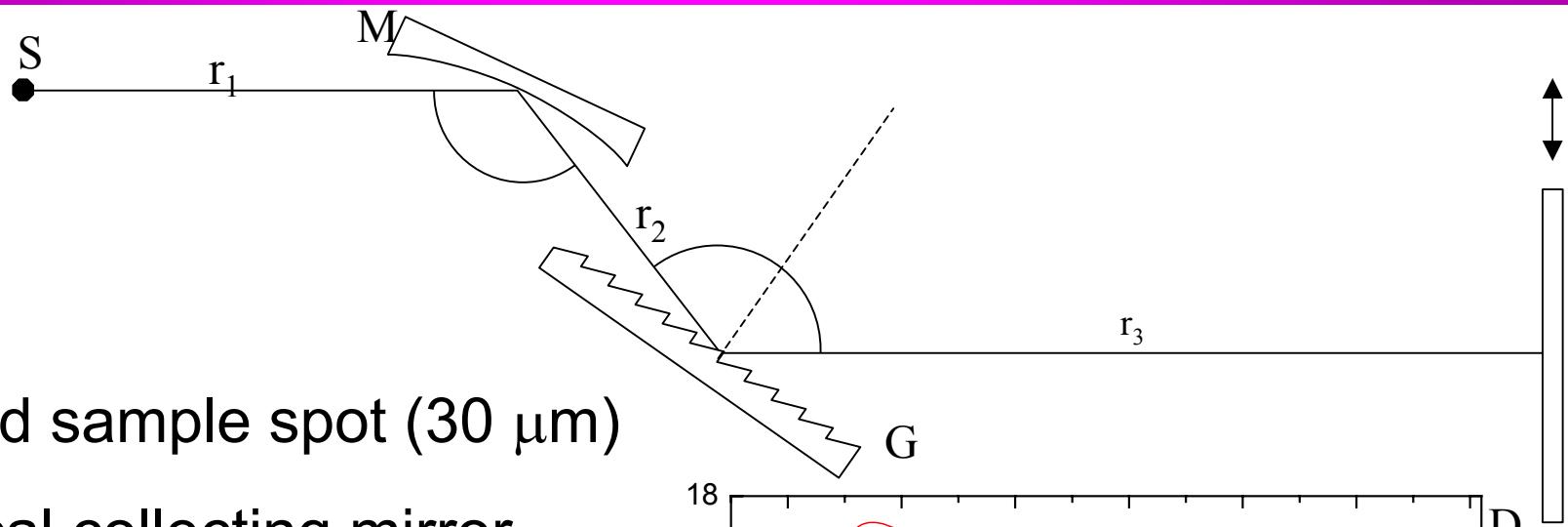


RIXS of liquid water

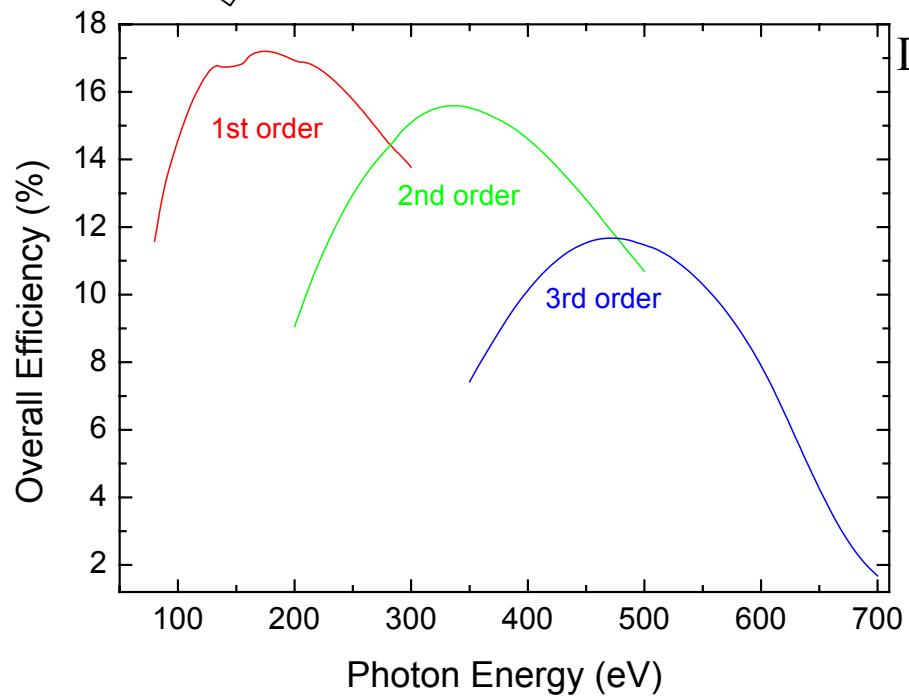
- Distinct spectral differences between H_2O and D_2O in RIXS



Design of a high-efficiency soft x-ray spectrometer



- Focused sample spot ($30 \mu\text{m}$)
- Spherical collecting mirror
- VLS plane grating
- CCD soft x-ray detector
- Simultaneously optimized for $\text{S L}_{2,3}, \text{C K}, \text{N K}, \text{O K}$
- High efficiency, $R \sim 1000$



Motivation for RIXS of Be-Chalcogenides

- How to learn something about the (buried) bulk band structure of insulators and powders ?
- Material system:
Be-Chalcogenides (BeSe, BeTe, BeS, BeO)
for applications in optical and spintronic devices
 - „photon-in-photon-out“ → bulk sensitive
 - k-conservation → band structure
 - Raman scattering, core excitons, and dephasing
 - buried interfaces: protection layers, surface oxidation

Spin-Aligner made of BeMnZnSe

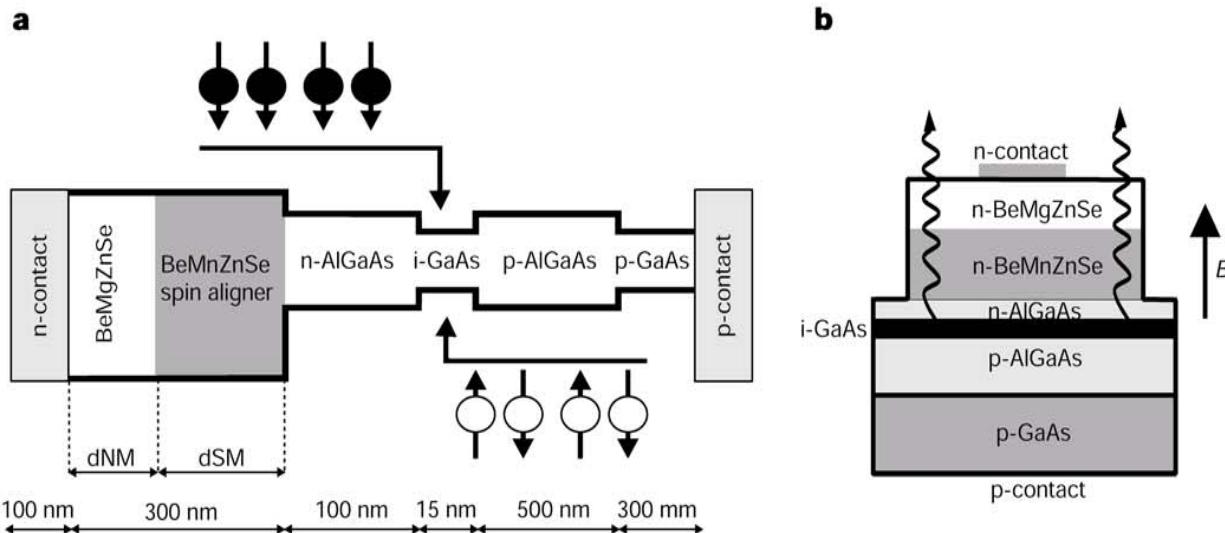


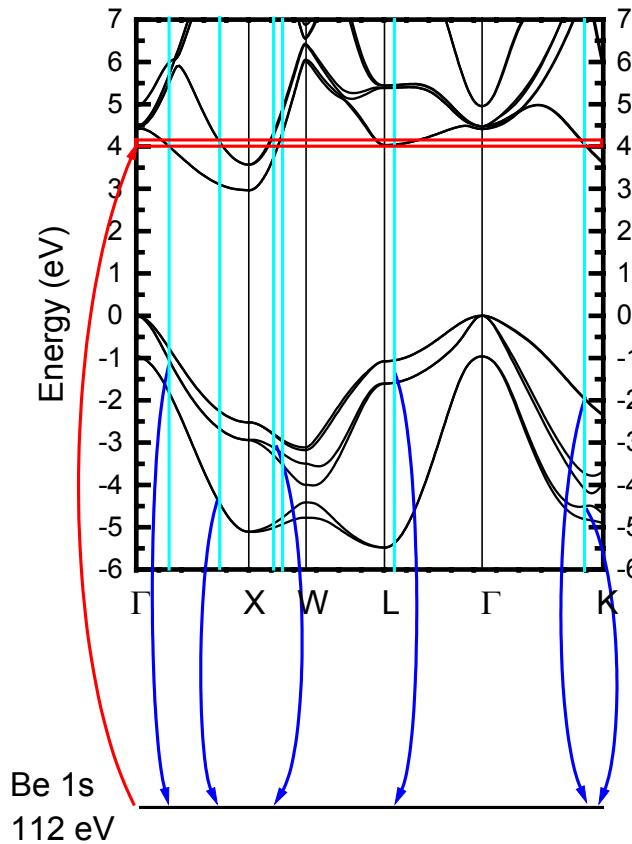
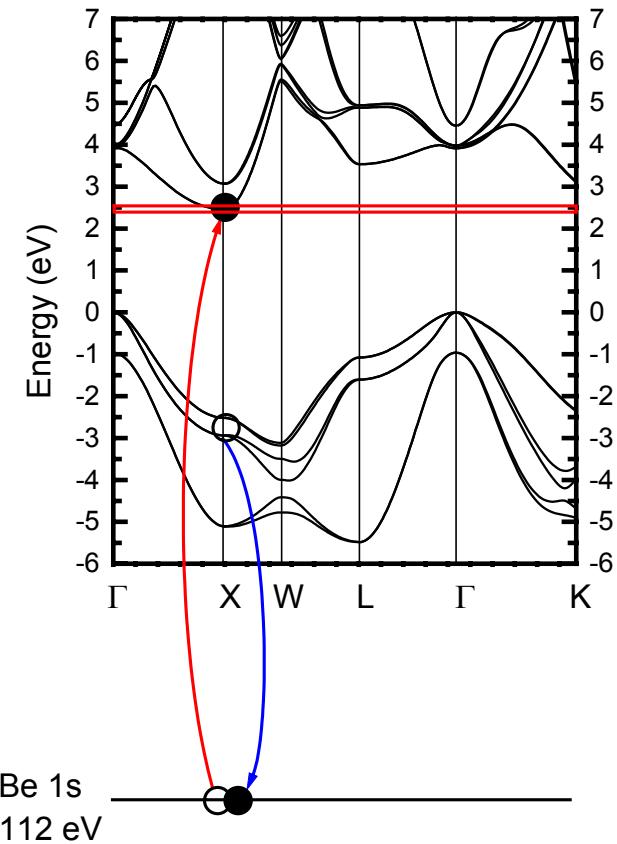
Figure 2 Device geometry and electric band structure. **a**, Schematic band structure of the spin-aligner light-emitting diode. Spin-polarized electrons are injected from the left into

the active GaAs layer, unpolarized holes from the right. **b**, Side view of the device showing the direction of the magnetic field and the emitted light.

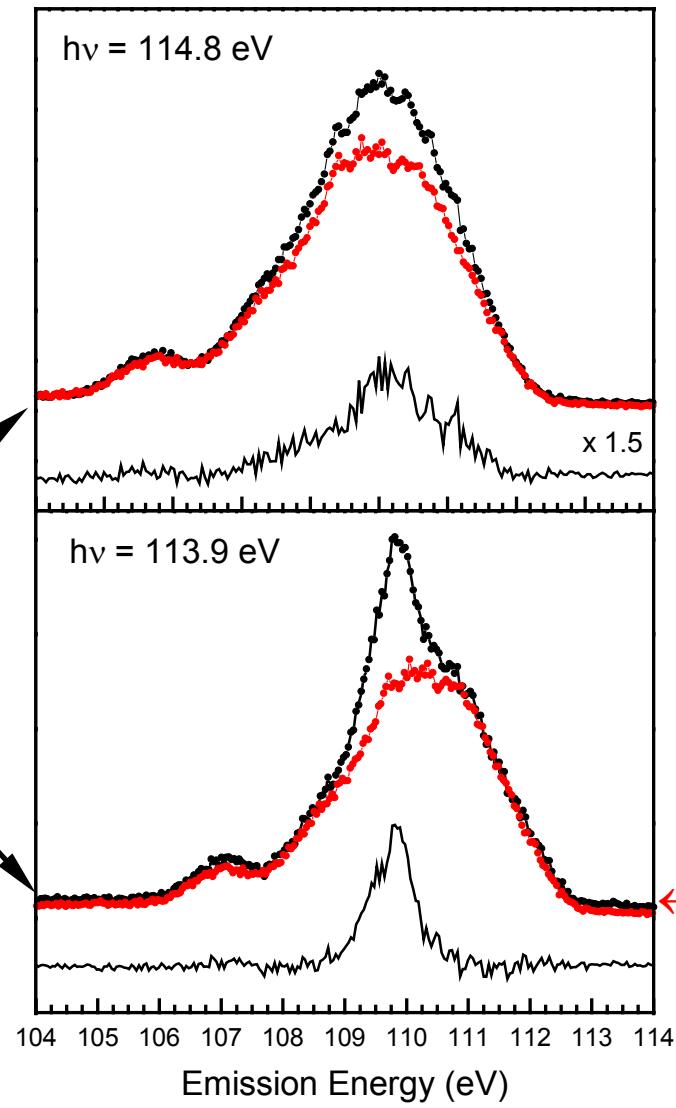
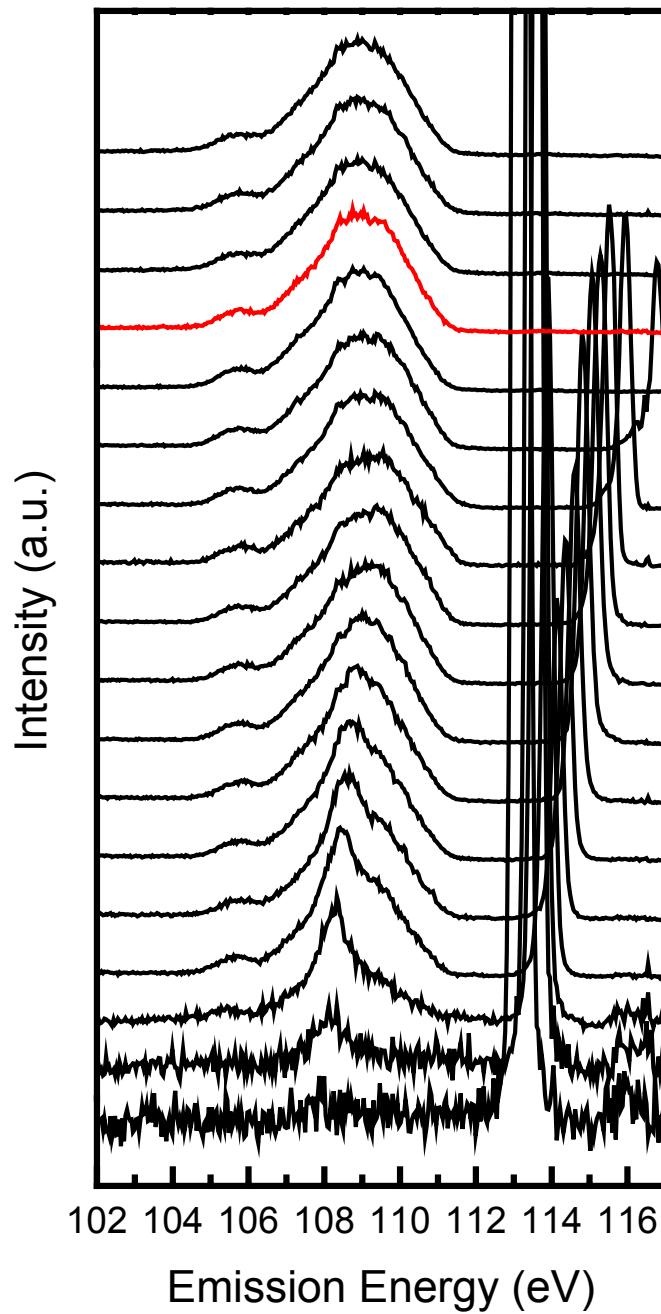
Electron spin polarization of almost 90 % !
(at 1.5 T and 1.5 K)

Theoretical description: Kramers-Heisenberg formalism

$$\frac{d\sigma}{d\Omega} \propto \sum_f \left| \sum_m \frac{\langle f | \vec{p} A | m \rangle \langle m | \vec{p} A | i \rangle}{E_m - E_i - \hbar\omega_{in} - i\Gamma_m/2} \right|^2 \delta(\hbar\omega_{in} - \hbar\omega_{out} - E_f + E_i)$$



RIXS of BeTe under a 20 nm ZnSe cap layer

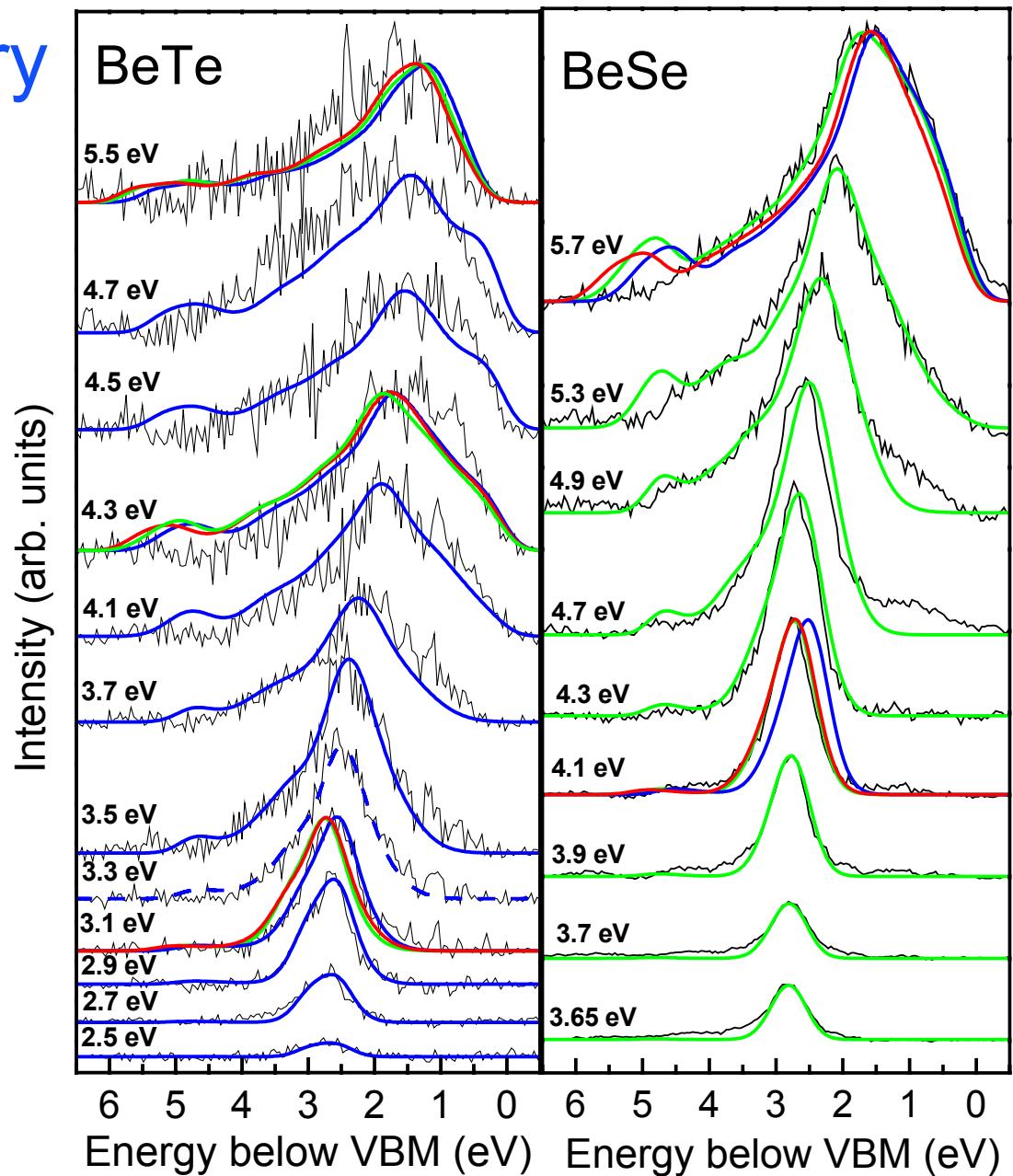


Comparison Experiment - Theory

EXX

LDA with
pseudopotential

LDA with
core hole



Beryllium sulfide (BeS)

Problems:

- very large band gap:

theory: 4.7 eV indirect, 7.4 eV direct

our experiment: 4.1 eV indirect, 7.4 eV direct (± 0.1 eV)
→ charging

- only available in powder form

→ no macroscopic orientation

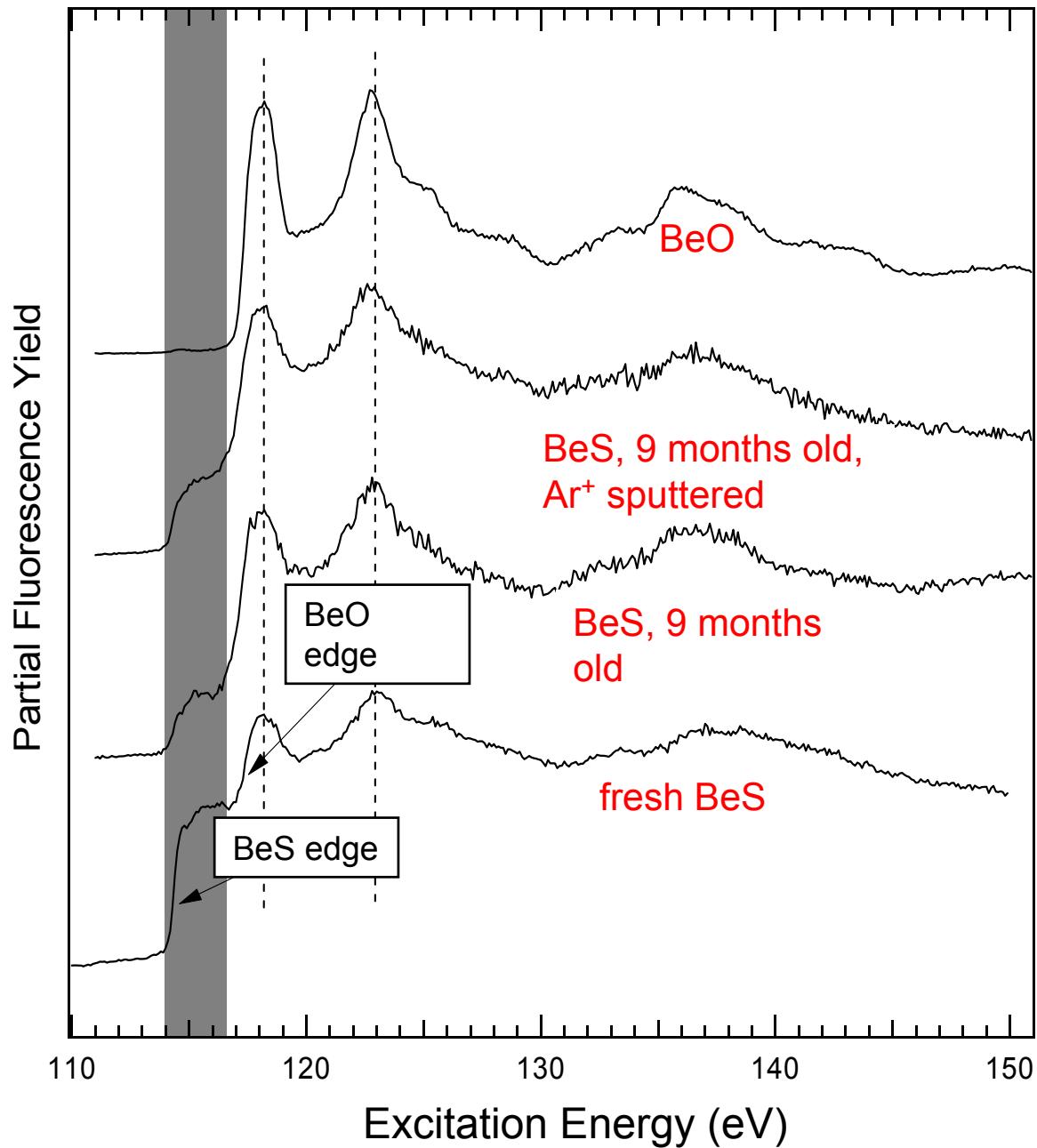
- easy to oxidize: $\text{BeS} + \text{H}_2\text{O} \rightarrow \text{BeO} + \text{H}_2\text{S}$

→ oxidized surface (approx. 150 nm !)

Task: learn about the band structure (so far: only theory!)

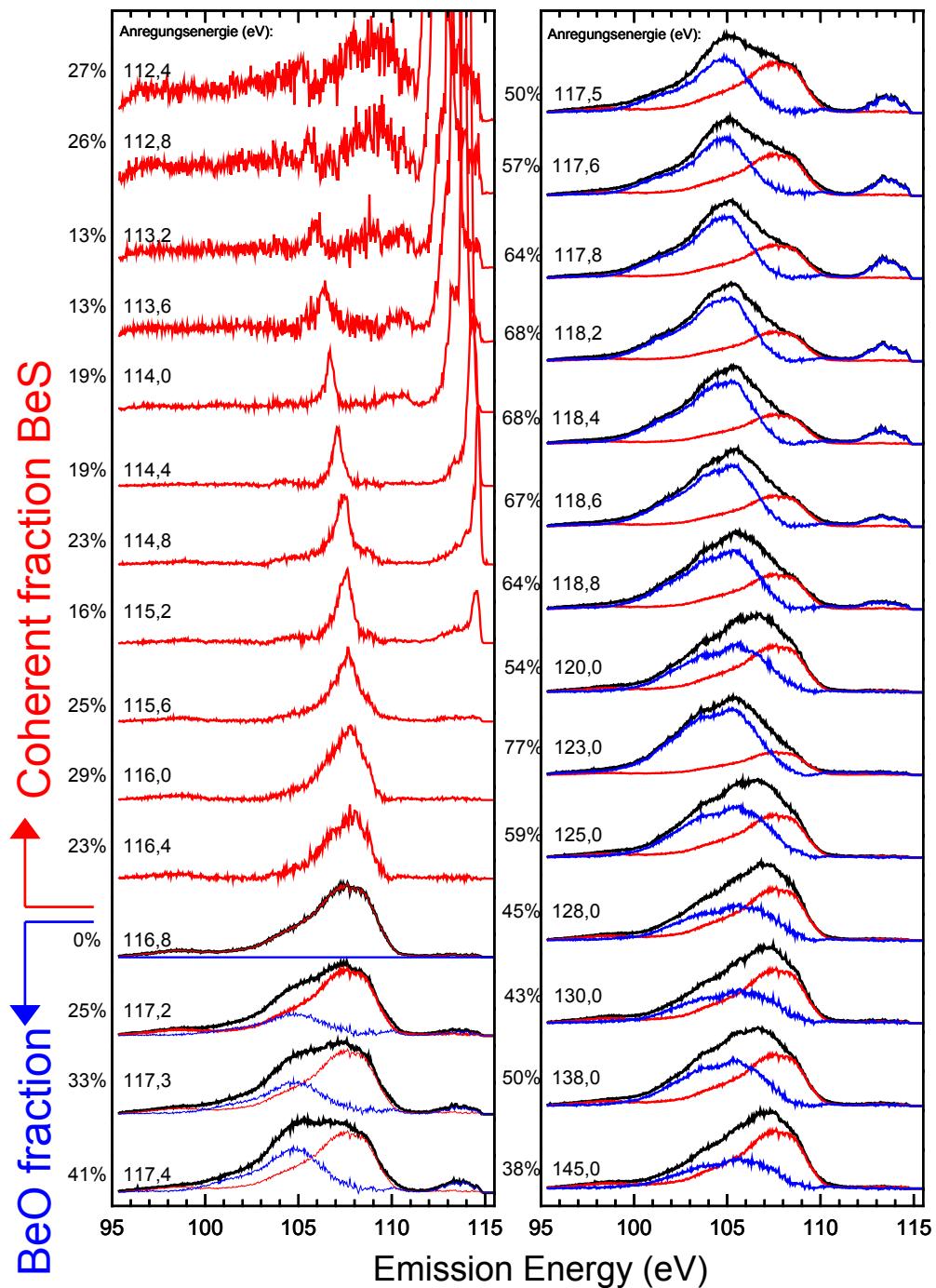
X-ray absorption of BeS powder

- Good luck: BeO has an even bigger band gap !
- Allows BeS to be probed in the gray energy window !



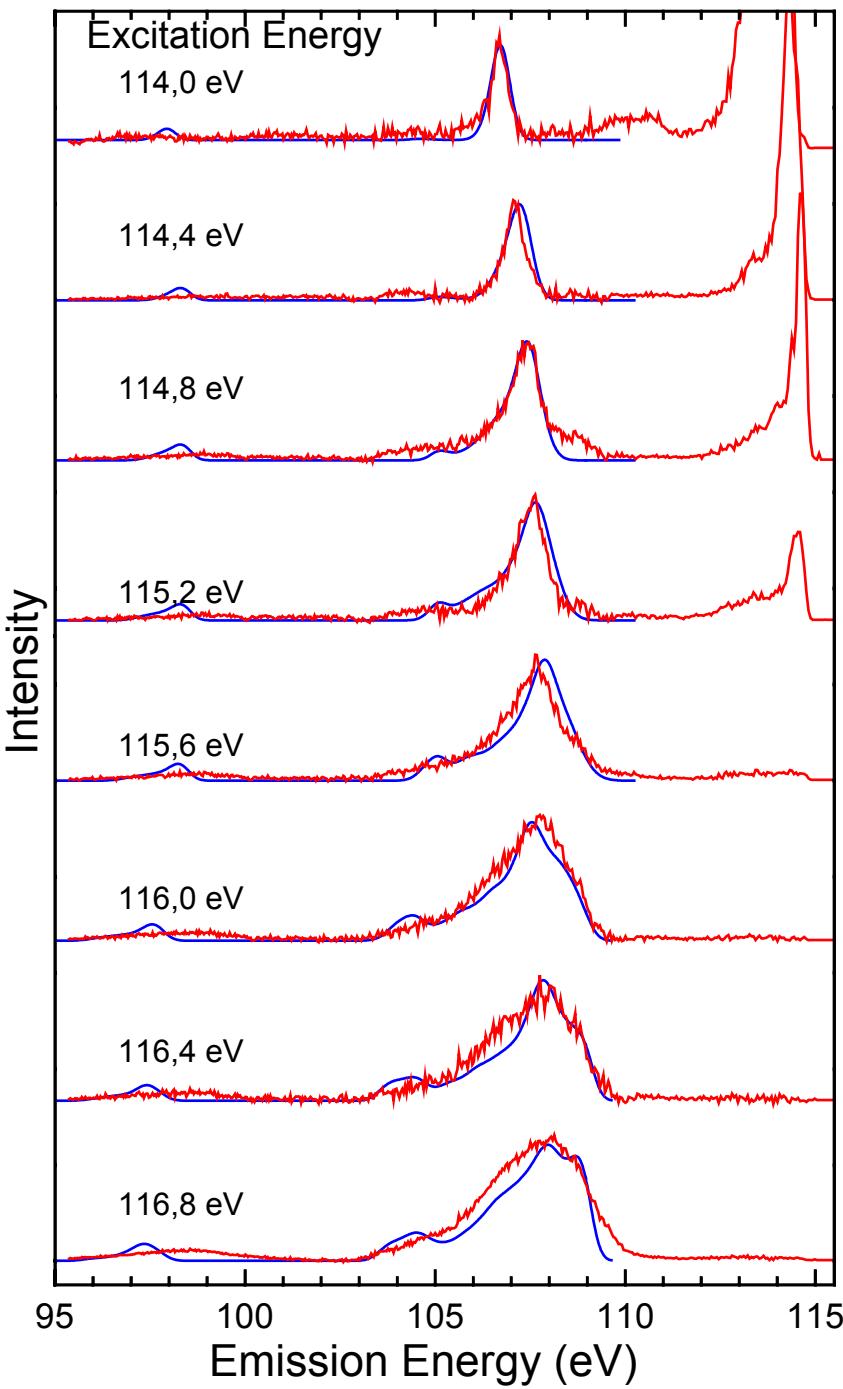
RIXS of BeS powder

- Band structure effects also visible for powder ($< 150 \mu\text{m}$) !
- Surface oxidation leads to BeO formation
→ approx. 150 nm thick !
- Cross sections strongly depend on excitation energy



RIXS of BeS-Powder

Comparison of Experiment and Theory



Summary

X-ray emission spectroscopy allows the investigation of

- Buried interfaces
 - atom-specific and chemically sensitive
 - variety of effects: reactions, intermixing, impurities, ...
- Buried bulk band structures
 - of wide-gap materials, insulators, powders
 - X-ray Raman scattering, core excitons, ...
- a variety of novel fields of application
 - "conventional", organic, biological, wet, ...